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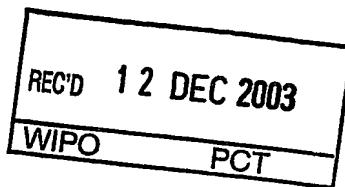


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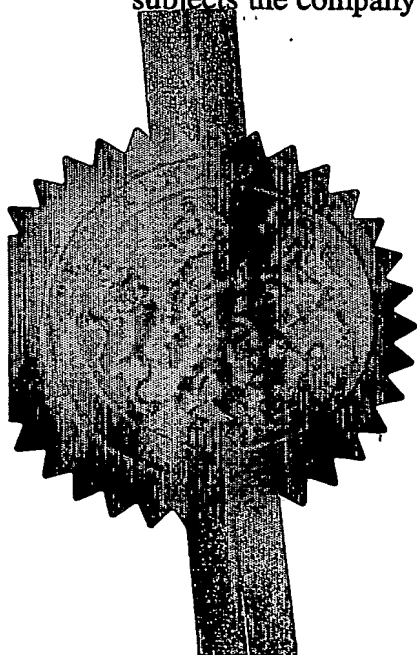
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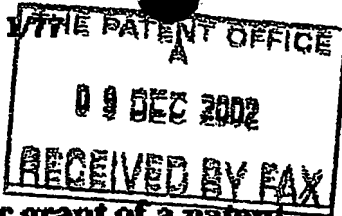
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Cardiff Road  
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P101523GB

**2. Patent application number**

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0228576.5

**3. Full name, address and postcode of the or of each applicant (underline all surnames)**Doncasters Limited  
Paralloy House  
Nuffield Road  
Billingham  
TS23 4DA  
UNITED KINGDOM

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

8492837002  
UNITED KINGDOM**4. Title of the invention**

HIGH TEMPERATURE ALLOYS

**5. Name of your agent (if you have one)**

Harrison Goddard Foote

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Fountain Precinct  
Leopold Street  
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0225648.5

04/11/02

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Description 15

Claim(s) 9

Abstract 1

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Statement of inventorship and right to grant of a patent (Patents Form 7/77) 1

Request for preliminary examination and search (Patents Form 9/77)

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0114 274 3704

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**Patents Form 1/77**

### High Temperature Alloys

This invention relates to high temperature alloys, and more particularly to an oxide dispersion strengthened  
5 nickel-chromium-iron alloy having improved creep resistance and oxidation resistance at high temperatures.

Frequently alloy materials for use at high temperatures, for example, alloy tubes used in ethylene pyrolysis and  
10 in steam methane reforming, suffer from insufficient creep resistance. The industry continues to look for improved materials and other technologies to enable more efficient ethylene production under increasingly severe  
pyrolysis/cracking conditions (higher temperatures,  
15 shorter residence times, and lower partial pressures of product), leading to increased ethylene yields. Current alloys have specific issues related to their creep performance which causes failure at increasingly high  
design process temperatures. This is the case currently  
20 for both castable alloy tubes and wrought alloy tubes.

An example of a known alloy material is INCOLOY® alloy 803 (UNS S 35045), which is an iron-nickel-chromium alloy specifically designed for use in petrochemical, chemical  
25 and thermal processing applications. The composition of INCOLOY 803, by weight, is 25%Cr, 35%Ni, 1%Mn, 0.6%Ti, 0.5%Al, 0.7%Si, 0.07%C and balance Fe. Relatively unsuccessful efforts have been made to improve the properties of this alloy by the addition of further  
30 alloying components and also by cladding.

It has been known for about thirty years that alloy creep resistance can be considerably improved by adding a fine dispersion of oxide particles into a metallic matrix,  
35 yielding a so-called oxide dispersion strengthened (ODS)

alloy. Such alloys show a creep threshold, that is to say, below a certain stress their creep rate is very low. This behaviour is commonly explained by interfacial pinning of the moving dislocations at the oxide particle;

5   Bartsch, M., A. Wasilkowska, A. Czyrska-Filemonowicz and U. Messerschmidt *Materials Science & Engineering A* 272, 152-162 (1999). It has recently been proposed to provide oxide dispersion strengthened clad tubes based on INCOLOY 803, but to date no entirely successful commercial

10   product is available  
([www.oit.doe.gov/imf/factsheets/mtu tubes](http://www.oit.doe.gov/imf/factsheets/mtu_tubes)).

According to the present invention, an improved creep resistant nickel-chromium-iron alloy comprises up to

15   about 5% of hafnium-containing particles. The alloy is particularly useful in the production of creep resistant tubes.

Also according to the invention, an improved oxide

20   dispersion strengthened nickel-chromium-iron alloy is provided, which comprises up to about 5% of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles.

25   In a first aspect, the present invention provides an oxide dispersion strengthened nickel-chromium-iron alloy comprising, by weight:

	Carbon	0.01 - 0.5%
30	Silicon	0.1 - 2.5%
	Manganese	0 - 2.5%
	Nickel	15 - 50%
	Chromium	20 - 40%
	Molybdenum	0 - 1.0%
35	Niobium	0 - 1.7%

3

	Titanium	0 - 0.5%
	Zirconium	0 - 0.5%
	Cobalt	0 - 2.0%
	Tungsten	0 - 1.0%
5	Hafnium	0.01 - 4.5%

balance iron and incidental impurities,

10 with the proviso that at least one of niobium, titanium and zirconium is present and that at least part of the hafnium is present as finely divided oxidised particles.

15 In a second aspect, the present invention provides a method of manufacturing an oxide dispersion strengthened nickel-chromium-iron alloy which comprises adding finely divided hafnium particles to a melt of the alloy before pouring, under conditions such that at least part of the hafnium is converted to oxide in the melt.

20 Preferred alloys according to the invention include the following compositions, where all percentages are given by weight:

TABLE 1

	Carbon	Silicon	Manganese	Nickel	Chromium	Molybdenum
A	0.3 - 0.5	0.1 - 2.5	2.5 max	30 - 40	20 - 30	1.0 max
B	0.03 - 0.2	0.1 - 2.5	2.5 max	30 - 40	20 - 30	1.0 max
C	0.3 - 0.5	0.1 - 2.5	2.5 max	40 - 50	30 - 40	1.0 max
D	0.03 - 0.2	0.1 - 2.5	2.5 max	40 - 50	30 - 40	1.0 max
E	0.30 - 0.5	0.1 - 2.5	2.5 max	19 - 22	24 - 27	1.0 max
F	0.03 - 0.2	0.1 - 2.5	2.5 max	30 - 45	19 - 22	1.0 max

25

	Niobium	Hafnium	Titanium	Zirconium	Cobalt	Tungsten
A	1.7 max	0.025 - 4.5	0.5 max	0.5 max	2.0 max	1.0 max
B	1.7 max	0.025 - 4.5	0.5 max	0.5 max	2.0 max	1.0 max
C	1.7 max	0.025 - 4.5	0.5 max	0.5 max	2.0 max	1.0 max
D	1.7 max	0.025 - 4.5	0.5 max	0.5 max	2.0 max	1.0 max
E	1.7 max	0.025 - 4.5			2.0 max	1.0 max
F	1.7 max	0.025 - 4.5	0.5 max	0.5 max	2.0 max	1.0 max

balance iron and incidental impurities.

The amount of hafnium in the alloy, by weight, is preferably from 0.05 to 3.0%, more preferably from 0.1% to 1.0% and most preferably from 0.2 to 0.5%. Preferably the hafnium is present in the alloy in the form of finely divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less, more preferably from 5 microns to 0.25 microns or less.

A particularly preferred alloy composition according to the invention consists essentially of the following components, by weight:

15	Carbon	0.45%
	Silicon	1.3%
	Manganese	0.9%
	Nickel	33.8%
20	Chromium	25.7%
	Molybdenum	0.03%
	Niobium	0.85%
	Hafnium	0.25%
	Titanium	0.1%
25	Zirconium	0.01%
	Cobalt	0.04%
	Tungsten	0.01%
	Iron	balance.

Incidental impurities in the alloys of the invention can comprise, for example, aluminium, phosphorus, sulphur, vanadium, zinc, arsenic, nitrogen, tin, lead, copper and cerium, up to a total amount of about 1.0% by weight.

In the method of the invention, it is important to provide conditions in the melt which permit oxidation of the hafnium particles without allowing detrimental reactions which would result in the hafnium being taken up in the slag. The correct oxidising conditions can be achieved by appropriate adjustment or additions of the components, especially silicon, and by ensuring that unwanted contaminants such as aluminium are absent or kept to a minimum. If the slag is able to react with the oxidised hafnium particles this of course removes them detrimentally from the melt. The level of oxygen in the melt can be varied by micro-additions of, for example, one or more of silicon, niobium, titanium and zirconium, and the optimum free oxygen level necessary to react with the hafnium particles can readily be found by routine experimentation.

After the reaction of the hafnium particles with free oxygen, alloying amounts of titanium and/or zirconium may be added, up to the specified limits of 0.5% by weight. The substantial removal of available free oxygen from the melt helps to ensure that any such titanium and zirconium additions do not form oxides, which could react detrimentally with the hafnium particles and reduce the yields of titanium, zirconium and hafnium present in the alloy.

It is important that the hafnium is added to the melt as finely divided particles and that it is oxidised in situ.



Attempts to add large pieces of hafnium to nickel/chromium micro-alloys have revealed that the hafnium does not disperse, but settles to the bottom of the alloy melt, or reacts with carbon resulting in a decrease of the alloy properties. Surprisingly, we have also found that the addition of hafnia (hafnium oxide) particles directly to the melt does not provide the desired dispersion strengthening either. Hafnia added in this way simply goes into the slag. According to the invention it has been found that it is necessary to carry out the oxidation of the hafnium particles in the melt in order to obtain the desired improvement.

The charge make up can be a virgin charge (pure metals), a mixture of virgin charge and reverts, a mixture of virgin charge and ingots, or a mixture of virgin charge and reverts and ingots. The ingots can be made from argon/oxygen decarburisation (AOD) revert alloy treatment or from in-house reverts treated by argon purging. In each case the chemical composition of the melt should be carefully monitored to avoid contaminants and the formation of unwanted slag. Special care should be taken to deslag the bath, and the maximum amount of slag is preferably removed from the surface of the bath. It is possible to improve slag removal by the use of a neutral deslag powder. If desired the melt can be maintained in an argon atmosphere, but this is not essential.

The melt temperature is preferably in the range of from 1580°C to 1700 °C, preferably from 1610 °C to 1670 °C.

Hafnium particles are preferably added to the melt just before pouring the molten alloy into the mould. If a ladle is used, the hafnium is preferably added in the

ladle. To improve the hafnium dispersion, the molten alloy is preferably stirred before pouring.

Any type of hafnium can be used, but electrolytic hafnium is preferred. The hafnium particles are preferably reduced in size as much as possible, for example, by grinding to a fine powder in a suitable mill. The hafnium particles preferably have a particle size of less than 5 mm, preferably less than 4 mm, with an average of from 1 to 2 mm. When dispersed in the melt, the hafnium particles are further reduced in size.

The alloys of the invention have a primary carbide network similar to the corresponding alloys without the oxide dispersion. The primary carbides are mainly composed of chromium and/or iron carbo-nitrides, optionally with niobium, titanium and/or zirconium carbo-nitrides also present. The invention also provides the possibility of obtaining a dispersion of secondary carbides after the alloy has been brought to a high temperature. These secondary carbides are mainly chromium (or other elements such as iron) carbo-nitrides and optionally niobium, titanium (and/or zirconium) carbo-nitrides.

In additions to these precipitates, the invention provides for the formation of a hafnia / hafnium oxide dispersion (the hafnium can be oxidised to form  $\text{HfO}_2$ , but it can be expected that there will also be formed a metastable oxide  $\text{HfO}_x$  with  $x$  as a variable), and hafnium/niobium/titanium carbo-nitrides and (rarely) oxides mixtures (the quantity of niobium and titanium is variable as well as the nitrogen and the oxygen).  $\text{HfO}_2$  can exist in three different crystallographic forms,  $\text{HfO}_2(\alpha)$  monoclinic (between ambient temperature and

1670°C,  $\text{HfO}_2$ (gamma) tetragonal (1670°C up to 2250°C) and  $\text{HfO}_2$ (beta) cubic (up to 2250°C). According to a further aspect of the invention, the  $\text{HfO}_2$  is preferably present as the (alpha) monoclinic form in the alloys of the invention.

It is also possible that some hafnium carbo-nitrides may be formed. More numerous titanium nitride (or carbide) dispersions may be observed in the alloy, some of which may also contain hafnia particles.

In another aspect, the invention provides an oxide dispersion strengthened nickel-chromium-iron alloy, which comprises up to about 5% of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles, the alloy having a carbon content of from 0.3% to 0.5% by weight and having an improved high temperature creep resistance, leading to an improved service life expectancy. Without wishing to be confined to any particular theory, it is believed that the creep resistance of the new alloys of this aspect of the invention derives from the ability of the particle dispersion to delay the motion of the dislocations in the alloy lattice. The micro-alloy, without the oxide dispersion, can delay the motion of dislocations by the presence of carbide (and/or nitride) precipitates, but the presence of the oxide dispersion provides a substantial unexpected extra improvement. An example of a high carbon oxide dispersion strengthened alloy is alloy A in Table 1.

In a still further aspect, the invention provides an oxide dispersion strengthened nickel-chromium-iron alloy, which comprises up to about 5% of hafnium, with at least part of the hafnium being present as finely dispersed

oxidised particles, the alloy having a carbon content of from 0.03% - 0.2%, preferably 0.03% - 0.1%, more preferably 0.03% - 0.08%, for example, about 0.05% - 0.07%, and a significantly increased service temperature, preferably greater than 1150°C. Without wishing to be confined to any particular theory, it is believed that the improved high temperature performance of the new alloys of this further aspect of the invention is due to the replacement of the strengthening carbide dispersion by a hafnia dispersion which is more stable than the carbide at high temperature. An example of a low carbon oxide dispersion strengthened alloy is alloy B in Table 1.

The alloys of the invention can be formed into tubes, for example, by rotational moulding, and such rotationally moulded tubes are a further aspect of the invention. The rotational moulding process can provide a non-uniform particle distribution in the tube wall, with the greater concentration of particles being towards the outer surface of the tube wall, and this can be beneficial in some cases. For example, in certain applications the internal bore of the tube is machined, removing 4-5 mm of material; this gradient of concentration ensures that the hafnium/hafnia reinforcement is kept in the useful part of the tube. Other components that can be manufactured from the new alloys include fittings, fully fabricated ethylene furnace assemblies, reformer tubes and manifolds.

A further advantage of the hafnium addition is that it can tend to improve the oxide layer adherence at the surface of an alloy tube. The alloy is able to develop an oxide layer on its surface that protects it against corrosion by carburisation. This protective oxide layer

10

is formed ideally of chromium/manganese/silicon oxides, but can also include iron and nickel oxides. The oxide layer has a tendency to spall during the tube service life (because of differences of coefficients of expansion with the alloy, compressive stresses in the oxide, etc). Spalling leaves the alloy unprotected against corrosion from the gaseous and particulate reactants of the ethylene cracking process. It has surprisingly been found that the hafnium addition can tend to delay the spalling of the protective oxide layer.

Embodiments of alloys according to the invention are illustrated in the accompanying Drawings, by way of example only, in which:

15

Figure 1 is a photomicrograph of a first alloy according to the invention with its composition;

Figure 2 is a photomicrograph of a second alloy according to the invention with its composition;

20 Figure 3 is a photomicrograph of a third alloy according to the invention with its composition;

Figure 4 is a photomicrograph of a fourth alloy according to the invention with its composition.

Figure 5 is a photomicrograph of a fifth alloy according to the invention; and

25 Figure 6 is a photomicrograph of a sixth alloy according to the invention.

The invention is further illustrated by the following Examples, in which all percentages are by weight:

#### Example 1

35 The following melt composition is produced in a clean furnace:

11

	Nickel	35%	
	Chromium	25%	
	Carbon	0.4%	
5	Niobium	0.8 - 0.9%	
	Silicon	1.6 - 1.8%	
	Manganese	1.1 - 1.3%	
	Iron and incidental impurities		balance.

10 The temperature of the melt is raised to a tap temperature of 1640°C to 1650°C and the silicon content checked. The furnace is then de-slaged, removing as much slag as possible. 100kg of alloy are then tapped into a ladle and 0.35% hafnium particles of particle size  
15 maximum 5 mm, average 1 -2 mm, are added to the tap stream. After the hafnium addition, 0.18% titanium, in the form of FeTi is added to the ladle.

The alloy in the ladle is stirred and immediately poured  
20 into a tube mould.

The creep resistance properties of the alloy thus produced were compared with the properties of an otherwise identical commercial alloy from which the  
25 hafnium addition was omitted.

The results of a Larson-Miller plot of the stress-rupture properties of the commercial alloy derived from the regression analysis of numerous creep tests gave a  
30 typical figure of 16.7 MPa at a temperature of 1100°C. The commercial alloy is expected to fail after a minimum of 100 hours, with a mean value failure of 275 hours. The alloy according to the invention had a minimum failure time of rupture of 370 hours and a mean value  
35 failure of 430 hours.

### Example 2

The procedure of Example 1 is repeated using the same  
5 melt composition except that the titanium addition is  
omitted.

The creep resistance properties of the alloy thus  
produced were compared with the properties of an  
10 otherwise identical commercial alloy from which the  
hafnium addition was omitted.

The results of a Larson-Miller plot of the stress-rupture  
properties of the commercial alloy derived from the  
15 regression analysis of numerous creep tests gave a  
typical figure of 16.2 MPa at a temperature of 1100°C.  
The commercial alloy is expected to fail after a minimum  
of 100 hours, with a mean value failure of 202 hours.  
The alloy according to the invention had a minimum  
20 failure time of rupture of 396 hours, a mean value  
failure of 430 hours and a maximum failure time of  
rupture of 629 hours.

The results of Examples 1 and 2 show the dramatic  
25 improvement in creep properties that can be obtained  
using the alloys and method of the invention.

### Example 3

30 This example describes the production of a low carbon  
oxide dispersion strengthened alloy according to the  
invention.

The following melt composition is produced in a clean  
35 furnace:

Nickel 33% - 35%  
 Chromium 24% - 26%  
 Carbon 0.04% - 0.08%  
 5 Silicon 1.0% - 1.2%  
 Manganese 1.0% - 1.2%  
 Molybdenum 0.14% - 0.3%  
 Iron and incidental impurities balance.

10 The temperature of the melt is raised to a tap temperature of 1640°C to 1650°C and the silicon content checked. The furnace is then de-slaged, removing as much slag as possible. 100kg of alloy are then tapped into a ladle and 0.75% hafnium particles of particle size  
 15 maximum 5 mm, average 1 -2 mm, are added to the tap stream. After the hafnium addition, 0.18% titanium, in the form of FeTi is added to the ladle.

20 The alloy in the ladle is stirred and immediately poured into a tube mould. The chemical composition of the tube alloy by spectrometer analysis is:

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti
0.07	1.0	0.91	32.9	25.5	0.20	0.03	0.30	0.17

Zr	Co	V
0.01	0.03	0.06

25

Traces (P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.24

A photomicrograph of the alloy is shown in Figure 5. The dispersed oxidised particles can clearly be seen.

30



## Example 4

The procedure of Example 3 is repeated using the same melt composition except that the hafnium addition is 0.5%. The chemical composition of the tube alloy by spectrometer analysis is:

C	S	Mn	Ni	Cr	Mo	Nb	Hf	Ti
0.07	1.00	0.98	32.6	25.8	0.20	0.04	0.50	0.1

Zr	Co	W
0.01	0.04	0.08

Traces ( P + S + V + Zn + As + N + Sn + Pb + Cu + Ce ) = 0.23

A photomicrograph of the alloy is shown in Figure 6. The dispersed oxidised particles can clearly be seen.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be

replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series  
5 of equivalent or similar features.

The invention is not restricted to the details of any foregoing embodiments. The invention extends to any novel one, or any novel combination, of the features  
10 disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

**CLAIMS**

1. An oxide dispersion strengthened nickel-chromium-  
5 iron alloy comprising, by weight:

	Carbon	0.01 to 0.5%
	Silicon	0.01 to 2.5%
	Manganese	0 to 2.5%
10	Nickel	15 to 50%
	Chromium	20 to 40%
	Molybdenum	0 to 1.0%
	Niobium	0 to 1.7%
	Titanium	0 to 0.5%
15	Zirconium	0 to 0.5%
	Cobalt	0 to 2.0%
	Tungsten	0 to 1.0%
	Hafnium	0.01 to 4.5%,

- 20 balance iron and incidental impurities,

with the proviso that at least one of niobium, titanium  
and zirconium is present and that at least part of the  
hafnium is present as finely divided oxide particles.

25

2. An alloy according to claim 1, having a carbon  
content of from 0.3 to 0.5% by weight.

3. An alloy according to claim 1, having a carbon  
30 content of from 0.03 to 0.2% by weight.

4. An alloy according to claim 1 or 2, having the  
following composition, by weight:

35	Carbon	0.3 to 0.5%
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17

	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	30 to 40%
	Chromium	20 to 30%
5	Molybdenum	1.0% max.
	Niobium	1.7% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
	Zirconium	0.5% max.
10	Cobalt	2.0% max.
	Tungsten	1.0% max.,
	Balance iron and incidental impurities.	

5. An alloy according to claim 1 or 3, having the  
15 following composition, by weight:

	Carbon	0.03 to 0.2%
	Silicon	0.1 to 0.25%
	Manganese	2.5% max.
20	Nickel	30 to 40%
	Chromium	20 to 30%
	Molybdenum	1.0% max.
	Niobium	1.7% max.
	Hafnium	0.01 to 4.5%
25	Titanium	0.5% max.
	Zirconium	0.5% max.
	Cobalt	2.05% max.
	Tungsten	1.0% max.,

30 balance iron and incidental impurities.

6. An alloy according to claim 1 or 2, having the  
following composition, by weight:

35	Carbon	0.3 to 0.5%
----	--------	-------------

18

	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	40 to 50%
	Chromium	30 to 40%
5	Molybdenum	1.0% max.
	Niobium	1.7% max.
	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
	Zirconium	0.5% max.
10	Cobalt	2.0% max.
	Tungsten	1.0% max.,

balance iron and incidental impurities.

- 15 7. An alloy according to claim 1 or 3, having the following composition, by weight:

	Carbon	0.03 to 0.2%
	Silicon	0.1 to 2.5%
20	Manganese	2.5% max.
	Nickel	40 to 50%
	Chromium	30 to 40%
	Molybdenum	1.0% max.
	Niobium	1.7% max.
25	Hafnium	0.01 to 4.5%
	Titanium	0.5% max.
	Zirconium	0.5% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.,

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balance iron and incidental impurities.

8. An alloy according to claim 1 or 2, having the following composition, by weight:

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	Carbon	0.3 to 0.5%
	Silicon	0.1 to 2.5%
	Manganese	2.5% max.
	Nickel	19 to 22%
5	Chromium	24 to 27%
	Molybdenum	1.0% max.
	Niobium	1.7% max.
	Hafnium	0.01 to 4.5%
	Cobalt	2.0% max.
10	Tungsten	1.0% max.,

balance iron and incidental impurities.

9. An alloy according to claim 1 or 3, having the  
15 following composition, by weight:

	Carbon	0.03 to 0.2%
	Silicon	0.1 to 2.5%
	Manganese	2.5% max
20	Nickel	30 to 45%
	Chromium	19 to 22%
	Molybdenum	1.0% max.
	Niobium	1.7% max.
	Hafnium	0.01 to 4.5%
25	Titanium	0.5% max.
	Zirconium	0.5% max.
	Cobalt	2.0% max.
	Tungsten	1.0% max.,

- 30 balance iron and incidental impurities.

10. An alloy according to any of the preceding claims,  
in which the amount of hafnium in the alloy, by weight,  
is from 0.01 to 3.0%.

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11. An alloy according to any of the preceding claims, in which the amount of hafnium in the alloy, by weight, is from 0.1% to 1.0%.

5 12. An alloy according to any of the preceding claims, in which the amount of hafnium in the alloy, by weight, is from 0.2 to 0.5%.

10 13. An alloy according to any of the preceding claims, in which the hafnium is present in the alloy in the form of finally divided oxidised particles having an average particle size of from 50 microns to 0.25 microns, or less.

15 14. An alloy according to any of the preceding claims, in which the hafnium is present in the alloy in the form of finally divided oxidised particles having an average particle size of from 5 microns to 0.25 microns, or less.

20 15. An alloy according to any of the preceding claims, in which the hafnium is present in the alloy in the form of finely divided particles comprising  $\text{HfO}_2(\alpha)$  monoclinic crystals.

25 16. An alloy having the following composition, by weight:

	Carbon	0.45%
	Silicon	1.3%
30	Manganese	0.9%
	Nickel	33.8%
	Chromium	25.7%
	Molybdenum	0.03%
	Niobium	0.85%
35	Hafnium	0.25%

21

Titanium 0.1%  
Zirconium 0.01%  
Cobalt 0.4%  
Tungsten 0.01%,

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balance iron and incidental impurities.

17. An alloy having the following composition, by weight:

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Carbon 0.07%  
Silicon 1.0%  
Manganese 0.91%  
Nickel 32.9%

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Chromium 25.5%  
Molybdenum 0.20%  
Niobium 0.03%  
Hafnium 0.30%  
Titanium 0.17%

20

Zirconium 0.01%  
Cobalt 0.03%  
Tungsten 0.06%,

balance iron and incidental impurities.

25

18. An alloy having the following composition, by weight:

Carbon 0.07%  
Silicon 1.0%  
Manganese 0.98%  
Nickel 32.5%

30

Chromium 25.8%  
Molybdenum 0.20%

35

Niobium 0.04%



22

	Hafnium	0.50%
	Titanium	0.12%
	Zirconium	0.01%
	Cobalt	0.04%
5	Tungsten	0.08%,

balance iron and incidental impurities.

19. An alloy according to any of the preceding claims  
10 substantially as described in Examples 1 to 4.

20. An alloy according to any of claims 1 to 18  
substantially as described in Examples 5 and 6.

15 21. A nickel-chromium iron alloy comprising up to about  
5% of hafnium-containing particles.

22. A method of manufacturing an oxide dispersion  
strengthened nickel-chromium-iron alloy which comprises  
20 adding finely divided hafnium particles to a melt of the  
alloy before pouring, under conditions such that at least  
part of the hafnium is converted to oxide in the melt.

23. A method according to claim 22, in which the alloy  
25 is an alloy as claimed in any of claims 1 to 21.

24. A method according to claim 22 or 23, wherein the  
hafnium particles have a particle size of less than 5mm.

30 25. A method according to any of claims 22 to 24, in  
which the amount of hafnium added to the melt is from  
0.01 to 3.0% by weight.

26. A method according to any of claims 22 to 25,  
35 wherein the hafnium particles are added to the melt

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shortly before pouring the molten alloy into the mould.

27. A method according to claim 26, in which the hafnium particles are added to the molten alloy in a ladle.

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28. A method according to any of claims 22 to 27, in which the hafnium is electrolytic hafnium.

29. A method according to any of claims 22 to 28, in which the alloy melt is substantially aluminium free.

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30. A method according to any of claims 22 to 29, wherein the level of oxygen in the melt is varied by additions of one or more of niobium, titanium and zirconium.

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31. A method according to claim 30, in which the titanium is added in the form of TiFe after the hafnium addition.

20

32. A method according to any of claims 22 to 31, in which the maximum amount of slag is removed from the surface of the alloy.

33. A method according to any of claims 22 to 32, in which the melt temperature is in the range of from 1580°C to 1700°C.

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34. A method according to any of claims 22 to 33, in which the alloy is formed into a tube by rotational moulding.

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35. A method according to any of claims 22 to 34 substantially as described in Examples 1 to 4.

35

36. A method according to any of claims 22 to 34 substantially as described in Examples 5 and 6.

37. A method of manufacturing a nickel-chromium-iron alloy, which comprises adding finely divided hafnium particles to the melt before pouring.

38. A creep resistant alloy tube formed from a nickel-chromium-iron alloy comprising up to about 5% of hafnium-containing particles.

39. A tube according to claim 38, which comprises an oxide dispersion strengthened nickel-chromium-iron alloy comprising up to about 5% of hafnium

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40. A nickel-chromium-iron alloy tube comprising up to about 5% of hafnium-containing particles substantially as hereinbefore described.

41. A tube formed from an alloy according to any of claims 1 to 21 by rotational moulding.

42. A nickel-chromium-iron alloy having a structure and composition substantially as described and illustrated in any one of Figures 1 to 4 of the accompanying Drawings, wherein the tables represent percentages by weight of the alloy constituents.

43. A nickel-chromium-iron alloy having a structure substantially as described and illustrated in Figures 5 or 6 of the accompanying Drawings.

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**ABSTRACT**

An improved creep resistant nickel-chromium-iron alloy comprises up to about 5% of hafnium-containing particles.

5 In one embodiment, an improved oxide dispersion strengthened nickel-chromium-iron alloy is provided, which comprises up to about 5% of hafnium, with at least part of the hafnium being present as finely dispersed oxidised particles.

10 The alloy is particularly useful in the production of creep resistant and high service temperature tubes.

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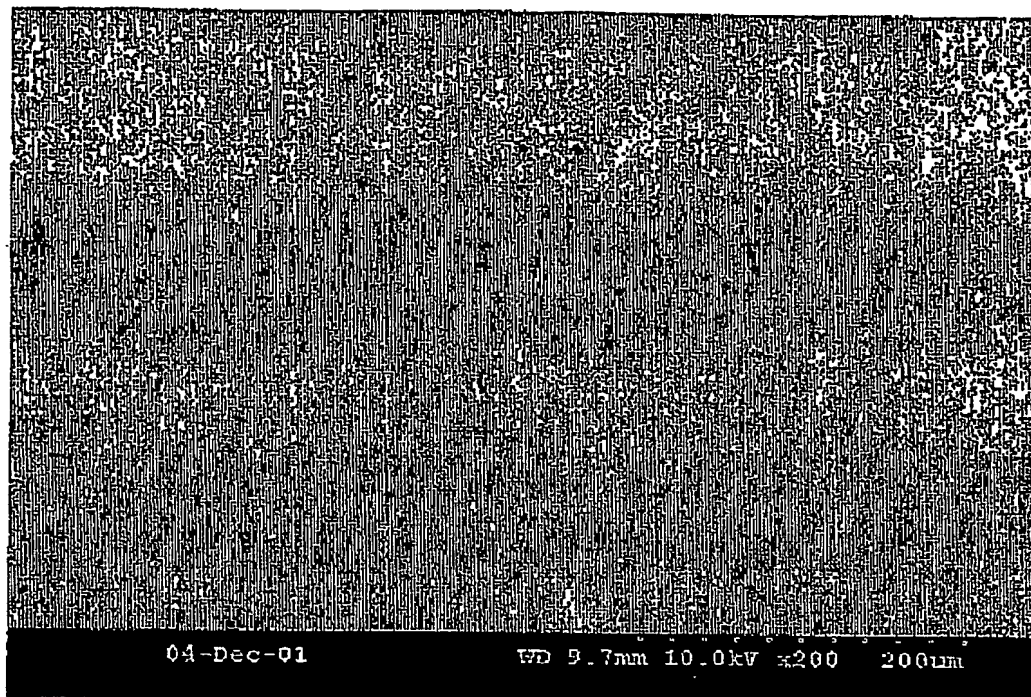


Figure 1

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.41	1.12	0.73	34.3	25.7	0.02	0.96	0.26	0.00	0.008	0.05	0.01

Traces (Al + P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.31

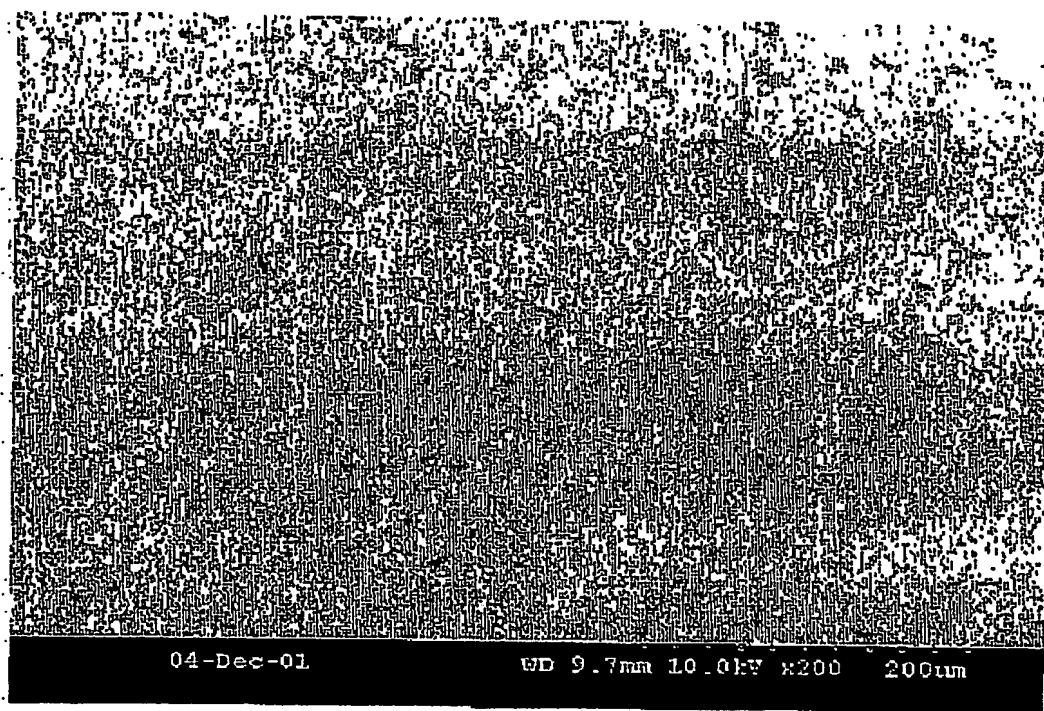


Figure 2

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.41	1.85	1.47	34.7	24.4	0.05	0.96	0.10	0.09	0.01	0.04	0.02

Traces (Al + P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.32

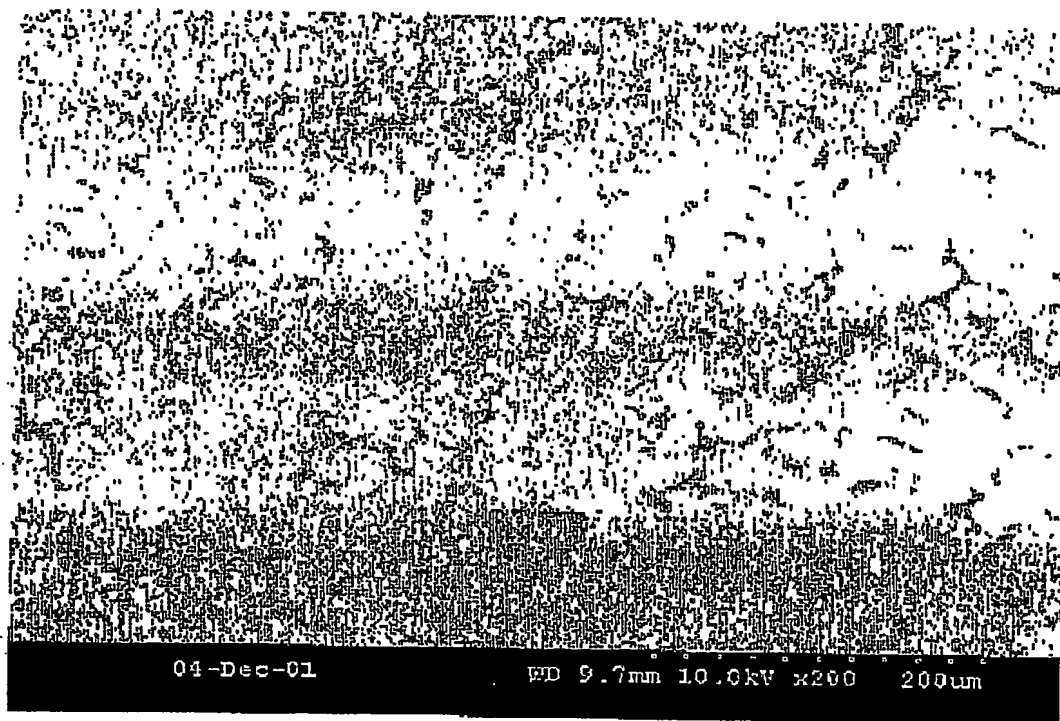


Figure 3

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.40	1.51	0.96	33.2	24.7	0.02	0.77	0.31	0.08	0.01	0.05	0.01

Traces (Al + P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.28

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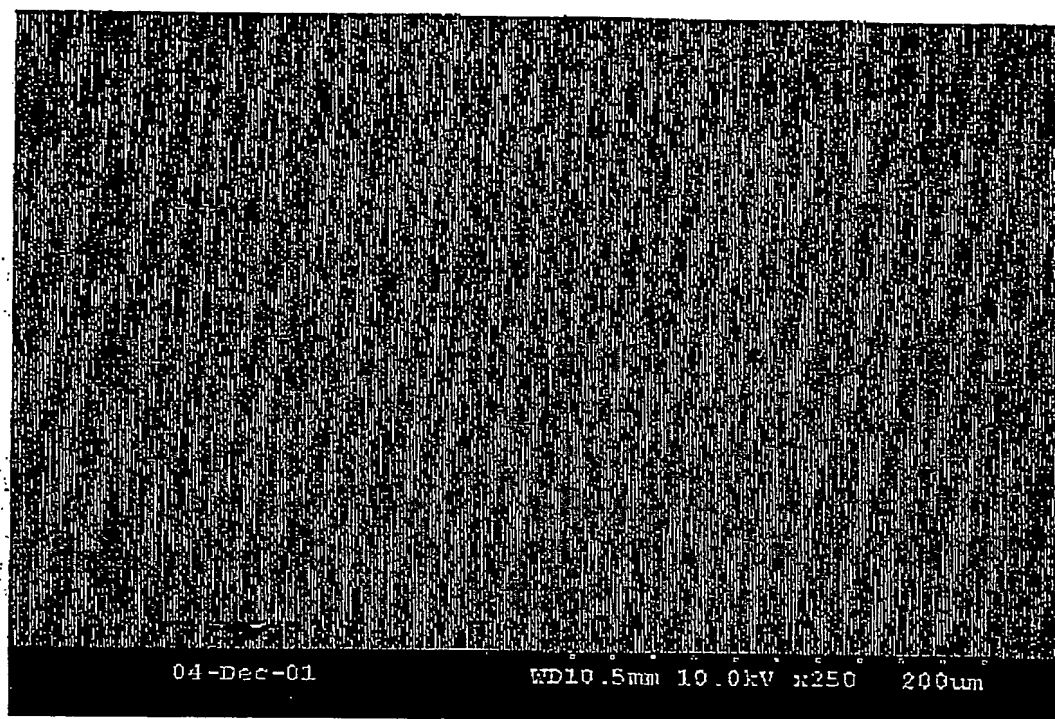


Figure 4

C	Si	Mn	Ni	Cr	Mo	Nb	Hf	Ti	Zr	Co	W
0.45	1.30	0.90	33.8	25.7	0.03	0.85	0.25	0.10	0.01	0.04	0.01

Traces (Al + P + S + V + Zn + As + N + Sn + Pb + Cu + Ce) = 0.29



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Figure 5

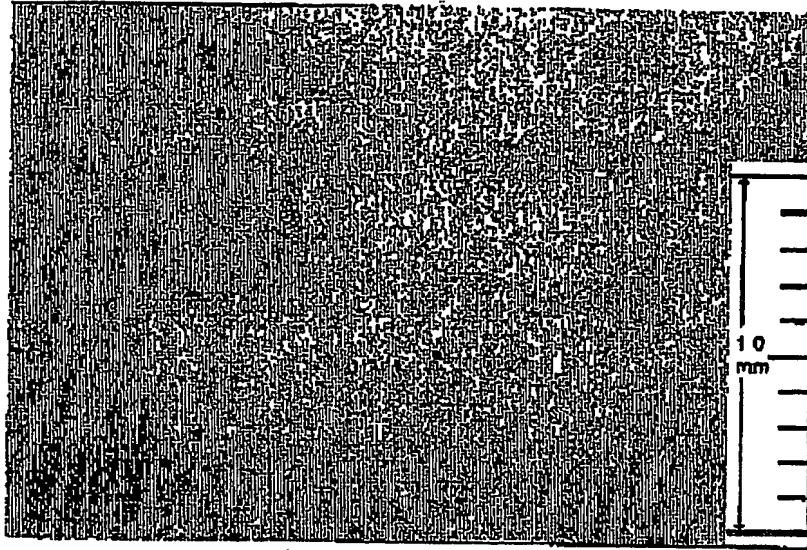
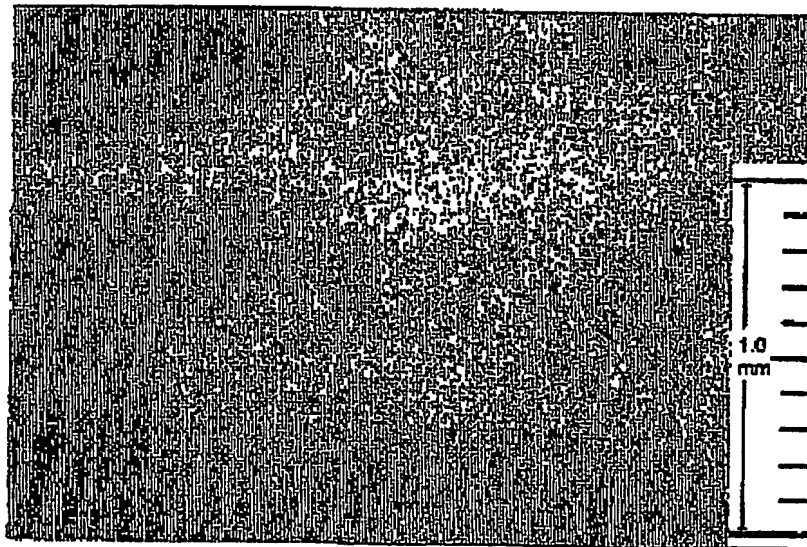


Figure 6



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